An improved fast-response vacuum-UV resonance fluorescence
CO instrument

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Abstract. The fast-response resonance fluorescence instrument for the airborne
measurement of carbon monoxide described by Gerbig et al. [1996] was modified by
implementing an improved optical filter with more efficient optics and an optimized
resonance lamp. Besides reductions in size and weight, the new instrument achieves a
sensitivity 10 times higher, a lower background (65 ppb compared with 250 ppb), and a
faster time response (<0.1 s) than the original instrument. The precision is ±1.5 ppb at an
atmospheric mixing ratio of 100 ppb CO, and the detection limit is 3 ppb (2σ) for an
integration time of 1 s. First results from the North Atlantic Regional Aerosol
Characterization Experiment (ACE-2) campaign during July 1997, when the new
instrument was deployed aboard the U.K. Meteorological Office C-130 aircraft, are used
to demonstrate the performance of the new instrument.

1. Introduction
Carbon monoxide has a strong influence on global tropo-
spheric chemistry [Fishman and Crutzen, 1978]. Anthropogenic
emissions constitute a major source of CO in the troposphere
[Seiler, 1974; Logan et al., 1981]. Further sources are the
oxidation of methane and hydrocarbons, as well as biomass burn-
ing [Crutzen and Andreae, 1990]. Because of its photochemical
lifetime of about 1 month in summer and its insolubility, CO is
an excellent tracer for investigating the transport of polluted
air masses into cleaner regions [Fishman and Seiler, 1983; Par-
rish et al., 1993]. Because of the stratospheric sink of CO it can
also be used to identify air masses of stratospheric origin [Hips-
kinson et al., 1987]. A large fraction of the transport of polluted
air masses may occur above the planetary boundary layer
(PBL), originating from exchange processes such as convection
between the polluted PBL and the free troposphere [Pickering
et al., 1992]. Thus aircraft measurements are needed in order
to obtain a better experimental database for estimating the
total amount of ozone and precursors that are transported
from continental sources into remote regions.

Techniques that have been used for in situ measurement of
CO aboard aircraft are (besides gas chromatography [see
Marenco, 1989], which provides only a discontinuous record)
the HgO method [Seiler et al., 1980], infrared absorption by gas
filter correlation (GFC) or nondispersive infrared spectroscopy
(NDIR) [Dickerson and Delany, 1987]), tunable diode
laser absorption spectroscopy (TDLAS) [Sachse et al., 1987;
Roths et al., 1996] and resonance fluorescence in the fourth
positive band of CO (hereinafter denoted VURF) [Volz and
Kley, 1985; Gerbig et al., 1996]. Only TDLAS and VURF ex-
hibit sufficient sensitivity and time response for precisely meas-
uring ambient CO mixing ratios at a time resolution of the
order of 1 s, as is required aboard aircrafts.

The VURF instrument that was originally built for balloon-
borne measurements of stratospheric CO [Volz and Kley, 1985]
was flown successfully aboard the Hercules C-130 after several
modifications [Gerbig et al., 1996]. These authors concluded on
the basis of laboratory experiments and theoretical consider-
ations that a large fraction of the observed background signal,
which determines the achievable precision and detection limit,
was not due to stray light, e.g. from the walls of the fluores-
cence chamber, but originated from continuum resonance Ra-
manscattering by oxygen molecules. This finding put a new
light on the required reduction of stray light as originally pro-
posed by Volz and Kley [1985] and opened the door for
a redesign of the instrument in order to improve its perfor-
mance. A further reason for the redesign was to make the
technique available to a wider scientific community, which was
realized in the framework of a technology transfer contract. In
this paper the new instrument is described, and a few examples
of measurements over the Atlantic during ACE2 are shown to
illustrate its performance.

2. The New Instrument
The new instrument is shown schematically in Figure 1. It
consists of the same principal components as the old instru-
ment, namely, a resonance lamp excited by a RF discharge, an
optical filter for selection of the appropriate wavelength inter-
val around 150 nm, which images the lamp into the RF cham-
ber, where the fluorescence is viewed at a right angle by means of
a photomultiplier tube (PMT) with suprasil optics. The
The combination of the above described changes increased the sensitivity of the instrument by a factor of 12 ($f = 5$ from the larger aperture of the optical filter, $f = 2$ from the improved PMT optics and the higher quantum efficiency, and the rest from the higher flux density of the lamp and reduced self-absorption in the discharge). The background signal decreased only by a factor of 3, leading to an increase in the signal-to-noise ratio by a factor of 5 (assuming a sample gas mixing ratio of 100 ppb CO). When expressed in CO equivalents (i.e., divided by the sensitivity), the background signal decreased to a value of 65 ppb, compared with 250 ppb for the version of the instrument described by Gerbig et al. [1996]. Reasons for the decrease of the background expressed in CO equivalents are the better discrimination of radiation in the wavelength region above 160 nm due to the narrower bandwidth of the filter (see Figure 2), and the better geometry of the imaging system leading to reduced stray light.

Further modifications were made to the fluorescence chamber in order to enhance the time resolution of the instrument. The dimensions of the original fluorescence chamber were changed to minimize stray light. With the limited pumping capacity provided by the four-stage membrane pump (Vacuubrand, MZ-4) installed aboard the C-130, this resulted in a relatively long exchange time of the sampled air in the illuminated volume, which limited the time resolution of the instrument to approximately 2 s, in accordance with the maximum possible time resolution given by photon statistics. With the improved sensitivity of the new instrument it was found advantageous to improve the gas kinetic time resolution of the instrument without having to install a larger pump in the aircraft. Although the sample gas is exchanged faster in the smaller and better defined fluorescing volume, the large dead volumes of the fluorescence chamber still disturb the time resolution. In order to further enhance the exchange rate of the sample gas within the fluorescing volume, a high-quality quartz tube was installed in the fluorescence cell (see Figure 1), coaxial with the optical axis of the exciting radiation. The increase in the background signal observed upon insertion of the quartz tube was only 10%.

A homogeneous flow through the quartz tube, without reducing the time response by dead volumes, is achieved by feeding the sample gas into the tube via eight small orifices around the window between optical filter and fluorescence chamber. The air is vented into the fluorescence chamber,
which is connected to the pump at the end of the light trap and at the PMT flange, in order to provide a well-defined air flow.

With the conservative assumption of a laminar flow profile in the quartz tube (the Reynolds number is about 1300), the residence time of the sample gas in the fluorescing volume which is imaged onto the cathode of the PMT (length ~ 1 cm) is calculated to be approximately 10 ms, at a pressure of 7.5 mbar and a volume flow rate of 1.4 L min⁻¹ as provided by the four-stage membrane pump used aboard the C-130. Experimentally, the time constant was determined to be <0.1 s, as limited by the 10 Hz sampling rate of the data acquisition system.

When using only the dielectric mirrors for wave length selection in the optical filter (grating used in zeroth order), Gerbig et al. [1996] observed a small positive interference by atmospheric water vapor, which overruled the expected negative interference due to absorption of the fluorescence radiation by water vapor. The positive interference was identified as being caused by photodissociation of H₂O at wavelengths below 135.7 nm and subsequent fluorescence of the excited OH radicals at wavelengths around 310 nm.

Figure 2 shows the absorption cross section of water vapor [Yoshino et al., 1996] together with the transmission of the optical filter used in the previous instrument (grating in zeroth order) and of the new optical filter. The dielectric mirrors used in the new optical filter provide a better discrimination of radiation in the wavelength region above 160 nm, where the fluorescence is detected, than the previously used filter. The new optical filter also provides about a factor of 7 better discrimination in the wavelength range below 136 nm. Indeed, no increase in the fluorescence signal was detected in laboratory tests, where water vapor was added to zero air (up to 100% relative humidity at 20°).

3. Laboratory Tests (Operating Conditions)

The influence of pressure changes in the whole system is shown in Figure 3. Since all flows are connected to the same pump, the pressure is the same for all volumes (i.e., fluorescence chamber, optical filter, and discharge lamp). The sensitivity shows a fairly broad maximum between about 7 and 11 mbar, while the background expressed in CO equivalents has a broad minimum between 5 and 7 mbar. This results in a broad maximum of the signal-to-noise ratio between 7 and 9 mbar. Most of the pressure dependence arises from the changes in the CO concentration (at constant mixing ratio) and from absorption of the exciting radiation due to O₂ in the fluorescence chamber [Volz and Kley, 1985].

Figure 4 shows the dependence of the sensitivity and the background signal (expressed in CO equivalents) on the CO₂/Ar flow rate through the new lamp at constant pressure (7.5 mbar). For very small flows, the sensitivity increases with increasing flow rate and reaches an almost constant value at flow rates of >5 mL (STP) min⁻¹. The background decreases with increasing flow and becomes also constant (within <5%) for flow rates >5 mL (STP) min⁻¹. The old lamp, because of its much larger volume, required flow rates of >40 mL (STP) min⁻¹ in order to reach optimum performance. Obviously, the smaller diameter of the lamp significantly reduces the residence time of the gas mixture in the discharge and thus the self absorption by ground state CO molecules that arise from the decomposition of the CO₂.

Figure 5 shows the dependency of the new instrument's sensitivity and background (expressed in CO-equivalents) on the N₂ flow in the optical filter at a constant pressure of 7.5 mbar. For nitrogen flow rates of <8 mL (STP) min⁻¹, both
sensitivity and background signal remain constant at levels of
58 cps ppb\(^{-1}\) and 84 ppb (CO equivalents), respectively. A
10% reduction in sensitivity and an increase of 7 ppb in the
background are observed when the flow rate is reduced to
about 1 mL (STP) min\(^{-1}\). Also shown in Figure 4 is the
corresponding signal-to-noise ratio calculated for a mixing ratio of
100 ppb CO. A flow rate of 5 mL (STP) min\(^{-1}\) was chosen for
the field measurements.

4. Flight Setup and Performance Assessment

The setup used for the airborne measurements aboard the
C-130 is shown in Figure 6. The sample gas is taken from the
starboard air sampling pipe (ASP) of the aircraft using a PFA
tube with 1/8 inch OD and a length of about 15 m. This
distance is determined by the only available position for the
instrument aboard the aircraft. The small residual influence of
water vapor due to absorption of the fluorescence radiation (a
mixing ratio of 2% H\(_2\)O causes a decrease in the fluorescence
signal of 10%) is removed by passing the sampled air over a
bed of Drierite (CaSO\(_4\) with humidity indicator) contained in
a 10-cm-long, 7-mm-ID Pyrex tube. Absorption of CO by the
drying agent was not observed within the experimental uncer-
tainties of 1%, and the response time of the instrument was not
measurably deteriorated.

Close to the ASP, a piezo-driven valve (Fa. Bürkert, model
6115) is installed in the inlet line. The valve is adjusted by the
program used for data acquisition and controls the pressure
inside the fluorescence chamber at 7.5 ± 0.1 mbar for ambient
pressures between 1013 and 175 mbar, which keeps the varia-
tion of the CO signal below 0.5%. The fluorescence chamber,
resonance lamp, and optical filter are connected to a four-stage
membrane pump (Vacubrand, model MZ4, all heads in series).
The gases for the lamp and the optical filter are contained in
two gas bottles, each with a volume of two liters. The filter is
continuously flushed with a flow of N\(_2\) (5 mL (STP) min\(^{-1}\),
purity 99.999%), which is purified from traces of CO, CO\(_2\),
and H\(_2\)O by passing it over a bed of hopcalite and molecular
sieve.

In situ calibration of the instrument is achieved by injecting
a standard (440 ppb CO in air) into the sampling line, close to
the control valve, at flow rates slightly higher than the sample
flow rate. The small excess flow (about 10 mL (STP) min\(^{-1}\)) is
vented into the ASP. The in-flight standard is compared with a
primary standard (1 ppm CO in air; Messer Griesheim) before
each flight. For determination of the background signal, the
 calibration standard is passed through a Hopcalite scrubber,
which quantitatively removes the CO to levels <1 ppb. In
addition, the background signal is determined by switching
a Hopcalite scrubber into the sample flow between the inlet
tube and the fluorescence chamber. This enables detection of
possible errors due to leaks within the inlet tube or the water
trap.

The resonance fluorescence signal depends on the pressures
in the chamber and in the lamp, as well as on the flow rates of
CO\(_2\)/Ar and nitrogen through the lamp and the optical filter,
respectively. The stability of these parameters is, therefore, of
importance for the accuracy of the measurement. The flow
rates of N\(_2\) and CO\(_2\)/Ar are held constant by (vacuum refer-
cenced) pressure regulators and thermostatted capillaries. Since
all flows are connected to the same pump, the pressure in the
lamp and in the optical filter are maintained constant at the
same level and with the same accuracy as the pressure in the
RF chamber by means of the piezo valve in the inlet line.

Changes in the temperature of the lamp and of the PMT
also have an influence on the instrument's sensitivity. The
photoemissive yield of the PMT's photocathode decreases with
temperature due to enhanced interaction of the photo elec-
trons with lattice photons, which leads to increased loss of
energy [Spicer and Wooten, 1963]. Laboratory testing showed a
temperature dependence of −0.9%/°C for the PMT sensitivity,
which is higher than the manufacturer's specification of
−0.2%/°C. The temperature of the lamp has an influence on
the sensitivity due to Doppler broadening of the lines and
changes in the rotational distribution of the CO emission.
More importantly, however, the output power of the radio
frequency circuit used for excitation of the discharge in the
lamp decreases significantly with increasing temperature.
Therefore the lamp and PMT module are thermostatted at a
were routinely performed about every 30 minutes. The behav-
ior of the sensitivity and the background during the whole
ACE-2 campaign and during the subsequent intensive flying
periods (TACIA and ACSOE) is shown in Figure 7, as a
function of accumulated flight hours. A slow decrease by a
factor of 2 can be seen during the first 140 flight hours, which
correspond to about 200 hours of operation including ground
tests and pre flight preparations. The decrease of sensitivity
was caused by a degradation of the lamp window. After re-
placement of the window, the sensitivity was restored to the
original value. In addition, the sealing rings were replaced
and the lamp was cleaned. No decrease of sensitivity was observed
during the following intensive flying campaign. The total range
in sensitivity and background changes for the individual flights
were 8% and 3.5 ppb, respectively. Since the changes occur
slowly, however, the deviation of the sensitivity and back-
ground from their interpolated value between consecutive cal-
ibration cycles are only ±1.3% and 0.9 ppb, respectively.

Figure 8 shows an example of the measurements made dur-
ing the second flight of the second Lagrangian experiment
during ACE-2 on July 17, 1997. During this flight, the C-130
flew rectangular box patterns at different altitudes, located at
36.5°N, 13.5°W, to the west of Sagres (Portugal). From 3-day
back trajectories it was indicated that the air masses which
were sampled during this flight period were likely influenced by
anthropogenic emissions over the Iberian peninsula. The mea-
surements shown in Figure 8 were made during the end of the
rectangular pattern at 900 m, during a short profile to 2000 m
and after a descent during the beginning of the next rectangu-
lar pattern at 1600 m. Fast and correlated changes in the
mixing ratios of CO and ozone occurred when the aircraft
changed the altitude, indicating a strong layering of different
air masses with a vertical extent of 100–300 m. From the right
panel of Figure 8 it can be seen clearly that the fluorescence
instrument is capable of following these rapid changes within
the time resolution of 1 s as determined by rate at which data
were recorded during these flights. The measurements made at
constant altitude also show a correlation between CO and ozo-
en on timescale of seconds, which corresponds to a hori-
zontal scale of a few hundred meters. The most likely expla-
nation is that the aircraft was flying close to the undulating
boundary between different air mass layers.

Also shown in Figure 8 are running averages over 60 s, which
were calculated from the original data in order to simulate an
instrument that has a less rapid response, e.g., a NDIR instru-
ment like the Thermo Instruments model 48S. It is clearly seen
that these averages do not show the rapid natural variations in
the CO mixing ratio. Most important, on many occasions the

5. Performance of the New Instrument

In Table 1 the specifications of the new version of the in-
strument flown aboard the C-130 are summarized and com-
pared to the old instrument [Gerbig et al., 1996]. The new
instrument achieves a much higher precision (determined by
counting statistics) due to the 12 times higher sensitivity and a
4 times lower background (in CO equivalents). The accuracy
is calculated from the accuracy of the calibration standard, the
background and sensitivity drift and from the achieved preci-
sion determined by counting statistics. Because of improved
temperature control of the critical components, background
and sensitivity are less influenced by changes in ambient con-
ditions, which leads to a better accuracy and requires less
frequent calibrations. The achievable time resolution is in-
creased from about 2 s to 0.1 s.

Since June 1997, the new instrument was deployed aboard the
U.K. Meteorological Office Hercules C-130 within several
European projects, i.e., the North Atlantic Regional Aerosol
Characterization Experiment (ACE-2), Testing of Atmo-
spheric Chemistry in Anticyclones (TACIA), and the U.K.
National Environmental Research Council project Atmo-
spheric Chemistry Studies in the Oceanic Environment (AC-
SOE). We show data from these experiments to demonstrate
the in-flight performance of the instrument and the long-term
stability.

In-flight calibrations and zeros lasting roughly 90 seconds
were routinely performed about every 30 minutes. The behav-
ior of the sensitivity and the background during the whole
ACE-2 campaign and during the subsequent intensive flying
temperature of 40°C, which is easy to maintain in the aircraft
environment.

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<th>Table 1. Comparison Between the Specifications of the Original and Improved Instrument</th>
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Figure 7. Average sensitivity and background signal for each flight during ACE-2 and following the TACIA and ACSOE intensive flying campaigns, plotted against the accumulated flight time. The bars indicate the maximum and minimum values for the individual flights. Note the offset of 50 ppb in the right panel.
distinct correlation with ozone is lost almost completely. This example clearly shows the advantage of a fast response instrument to investigate atmospheric structures on small spatial scales.

6. Conclusions

The new VURF instrument achieves a 5 times higher precision and a better time resolution (<0.1s) and is smaller in size and weight than the previous version. Data from flights during ACE-2 prove that the new instrument is able to resolve small scale natural variations in the CO mixing ratio with differences of 10 ppb within a second. The precision and time resolution of the new VURF instrument is comparable to that reached with TDLAS. Advantages of the VURF instrument, in particular for airborne measurements, are its smaller space and weight combined with less logistic demands compared to TDLAS.

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